

## **VERIFICATION OF TRANSLATION**

I, Shuji Sawada, of 2-34-1710, Heso 2-chome, Ritto-shi, Shiga 520-3031 Japan hereby declare that I am competent in both the Japanese and English languages and that the attached English language translation, which is identified as Docket No. 61A27500-A, is an accurate translation of Japanese Patent Application No. 2002-315726.

Date: April 5, 2010

signature: Shuji Sawada

[Name of Document]	Petition
[Docket Number]	61A27500-A
[Submission Date]	October 30, 2002
[Receiver]	Director General of the Patent Office
[IPC]	D01F 8/00
[Inventor]	
[Address or Residence]	c/o Mishima Plant, Toray Industries, Inc., 4845, Mishima-shi, Sizuoka
[Name]	Takashi OCHI
[Inventor]	
[Address or Residence]	c/o Mishima Plant, Toray Industries, Inc., 4845, Mishima-shi, Sizuoka
[Name]	Akira KISHIRO
[Applicant]	
[Identification No.]	000003159
[Address or Residence]	2-1, Nihonbashi-Muromachi 2-chome, Chuo-ku, Tokyo
[Name or Title]	TORAY INDUSTRIES, INC.
[Representative]	Sadayuki SAKAKIBARA
[Telephone Number]	077-533-8172
[Payment of Fee]	
[Record No.]	005186

[Amount to be paid]	¥21,000	
[Appendix]		
[Item]	Specification	1
[Item]	Drawing	1
[Item]	Abstract	1
[Need of Proof]	Yes	

[Name of Document]            Specification

[Title of the Invention]        POLYMER ALLOY FIBER

[Claims]

[Claim 1]    A polymer alloy fiber that has islands-in-sea structure consisting of two or more kinds of organic polymers of different levels of solubility, wherein the island component is made of a low solubility polymer and the sea component is made of a high solubility polymer, while the diameter of the island domains by number average is in a range from 1 to 100 nm, and 60% or more of the island domains have sizes in a range from 1 to 100 nm in diameter.

[Claim 2]    The polymer alloy fiber according to claim 1, wherein 60% or more of the island domains are in a section having a width of 30 nm in diameter of the island domains.

[Claim 3]    The polymer alloy fiber according to claim 1 or 2, wherein the sea component is made of a polymer that is highly soluble to an aqueous alkaline solution.

[Claim 4]    The polymer alloy fiber according to any one of claims 1 to 3, wherein the sea component is made of a polymer that is soluble to hot water.

[Claim 5]    The polymer alloy fiber according to any one of claims 1 to 4, wherein the island component polymer has a melting point of 165°C or higher.

[Claim 6]    The polymer alloy fiber according to any one of claims 1 to 5, wherein the Uster unevenness is 15% or less.

[Claim 7] The polymer alloy fiber according to any one of claims 1 to 6, wherein the strength is 2.5 cN/dtex or higher.

[Claim 8] A fibrous article that includes the polymer alloy fiber according to any one of claims 1 to 7 at least in part thereof.

[Claim 9] A method of manufacturing nanofibers having diameter by number average in a range from 1 to 100 nm, comprising dissolving the sea component polymer of the fibrous article according to claim 8.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a polymer alloy fiber that is preferably used as the precursor for nanofibers having small spread in single fiber fineness values.

[0002]

[Prior Art]

Polymers manufactured through polycondensation such as polyester typified by polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), and polyamide typified by nylon 6 (N6) and nylon 66 (N66) have been preferably used in such applications as clothes and industrial materials, because of the favorable mechanical properties and heat resistance of these fibers. Polymers manufactured through addition polymerization typified by polyethylene (PE) and

polypropylene (PP), in contrast, have been preferably used mainly in fibers for industrial applications, because of the favorable mechanical properties, resistance to chemicals and lightness of these fibers.

[0003]

The polyester fibers and the polyimide fibers, in particular, have been used in the applications for clothing articles and therefore have been subjected to vigorous researches for not only reforming the polymer but also improving the properties by controlling the cross sectional shape of the fiber or using an extremely fine fiber. One of such attempts resulted in ultrafine polyester fibers made by using an islands-in-sea multi-component fiber, that were used in an epoch making new product of synthetic leather having the touch of suede. These ultrafine fibers have been applied to the manufacture of ordinary clothes, and are used in the development of clothes that have excellent hands like peach skin which can never be obtained with ordinary fibers. Moreover, the ultrafine fibers have found applications not only for clothes but also for living wares such as wiping cloth and industrial materials, and have secured a position of its own in the area of synthetic fibers today. Recently, in particular, applications of the ultrafine fibers have been expanded to texturing cloth for the surface of a computer hard disk as described in Japanese Unexamined Patent

Publication No. 2001-1252 and Japanese Unexamined Patent Publication No. 2002-224945, and medical supplies such as cell adsorbing material as described in Japanese Unexamined Patent Publication No. 2002-102332 and Japanese Unexamined Patent Publication No. 2002-172163.

[0004]

Accordingly, there has been a demand for further finer fibers in order to make a synthetic leather of higher quality and clothes of excellent feeling. In the meantime, efforts are being made to increase the storage capacity of hard disks as the basis for the advance of IT industry. In order to increase the storage capacity of a hard disk with increased recording density, it is necessary to make the surface of the hard disk smoother from the mean surface roughness of 1 nm or more at the present to 0.5 nm or less. For this purpose, nanofibers having further decreased thickness have been required to make a texturing cloth for texturing the hard disk surface.

[0005]

However, the prior art islands-in-sea multi-component spinning technology has a limitation of 0.04 dtex (equivalent diameter 2  $\mu\text{m}$ ) for improving the single fiber fineness, which cannot fully meet the needs for the nanofibers. While there are methods for making ultrafine fibers from polymer blend fibers (Patent Documents 1, 2), a single fiber fineness that

can be achieved by these technologies is 0.001 dtex (equivalent diameter 0.4  $\mu\text{m}$ ) at the best, which also cannot fully meet the needs for the nanofibers. Moreover, while the single fiber fineness of the ultrafine fibers made by these methods is determined by the state of dispersion of the island polymer in the polymer blend fibers, the polymer blend system described in the patent document has a large spread of single fiber fineness values of the resultant ultrafine fibers due to insufficient dispersion of the island polymer in the polymer blend fibers. As a result, property of the product is determined by thick single fibers, failing to make full advantage of the properties of the ultrafine fibers and stabilize the product quality. In addition, when used as a texturing cloth for texturing the hard disk surface, the large spread of fineness values makes it impossible to support abrasive particles evenly on the texturing cloth, thus resulting in such a trouble that the use of the texturing cloth results in the hard disk surface becoming less smooth, contrary to the intention.

[0006]

Recently, for the purpose of making a precursor for carbon nanotube (CNT) by the polymer blend method, a method for manufacturing a fibrous material of polymer alloy is under development, wherein fine core-shell particles including a polymer that can be carbonized by firing (phenol



resin, etc.) as the shell and a matrix polymer that diminishes through pyrolysis are dry-blended and turned into thread-like form while retaining the fine dispersion structure obtained by dry blend, by melt extrusion at an extremely slow rate, with the thread-like polymer strings being bundled together and subjected to melt extrusion again, thereby to make the fibrous material of polymer alloy comprising the polymer, that can be carbonized by firing, being finely dispersed in the matrix polymer (Patent Document 3). However, since the combination of polymers described in the patent document inevitably requires the operation of firing, only CNT can be obtained and it is impossible to obtain a nanofiber made of an organic polymer. Also the control of the core-shell particles, which is a key point of the method, is carried out by spray drying of the shell polymer onto the core particles. With this process, since the core particles that are intrinsically spread in the diameter distribution, spread of the particle diameters becomes greater and the spread of diameters of the resultant CNT becomes very large (a collection of thin and thick carbon nanotubes). Also when the method is applied to the ordinary melt spinning process which is employed to process polyester, polyamide, polyolefin, etc. in the industry, although not described in detail in the publication, the core-shell particles fuse with each other at a position where the stream

of molten polymer is disturbed such as filtration, and therefore only coarsely dispersed polymer that can be carbonized can be obtained. As a result, it is necessary to avoid disturbing the state of dispersion achieved by dry blending as far as possible. But this requirement is impossible to meet in the current state of the spinning technology with the ordinary melt spinning process which is employed to process polyester, polyamide, polyolefin, etc. in the industry, and therefore the so-called candle spinning method must be employed wherein the polymer is extruded at an extremely slow rate directly from a barrel. With this spinning method, however, since the spinning rate is extremely low and the amount of discharge per unit time depends on the gas pressure applied to an extruding piston, the amount of discharge tends to be unstable and cooling unevenness tends to occur, thus resulting in a polymer alloy fibrous material having significant thick and thin unevenness in the longitudinal direction of the yarn. This results in further spread of diameters of the resultant CNT.

[0007]

There is also such a process employed to obtain core-shell particles of uniform particle size, as a suspension liquid of polymethacrylate (PMMA)/polyacrylonitrile (PAN) core-shell particles (about 200 to 600  $\mu\text{m}$  in diameter) prepared by two-stage soap-free polymerization and a

suspension liquid of PMMA particle are mixed and freeze-dried, and the polymer blend material thus obtained is used (Non-Patent Document 1). But this process also fails to produce a polymer alloy fibrous material that is uniform in the longitudinal direction of the yarn, due to the problem related to the melt spinning operation described above. Moreover, since there is no significant difference in solubility between the PMMA and the PAN, it is impossible to obtain a nanofiber made of an organic polymer. Also since the soap-free polymerization is restricted to radical polymerization, it cannot be applied to polymers manufactured through polycondensation such as polyester and nylon.

[0008]

As described above, there have been demands for nanofibers that have little spread of single fiber fineness values, which impose no restriction on the form of the fiber or the fibrous product and on the kind of polymer, and can be put in diverse applications, although a polymer alloy fiber constituted from polymers of different levels of solubility being dispersed on the order of nanometers has not been obtained as the precursor thereof.

[0009]

[Patent document 1]

Japanese Unexamined Patent Publication No. 3-113082 (pp.1-5)

[0010]

[Patent document 2]

Japanese Unexamined Patent Publication No. 6-272114 (pp.1-7)

[0011]

[Patent document 3]

Japanese Unexamined Patent Publication No. 2002-173308 (pp.1-6)

[0012]

[Non-Patent Document 1]

Functional Materials, vol.21, No. 11, 41-46 (2001)

[0013]

[Problems to be Solved by the Invention]

The present invention aims to provide a polymer alloy fiber constituted from polymers of different levels of solubility being dispersed on the order of nanometers therein, that can be used as a precursor for making nanofibers having little spread of single fiber fineness values, which can be put in diverse applications without any limitation on the form of the fiber or the fibrous articles and on the kind of polymer.

[0014]

[Means for Solving the Problems]

The object described above can be achieved by a polymer alloy fiber that has islands-in-sea structure consisting of two or more kinds of organic polymers of different levels of solubility, wherein the island component is made of a low

solubility polymer and the sea component is made of a high solubility polymer, while the diameter of the island domains by number average is in a range from 1 to 100 nm, and 60% or more of the island domains have sizes in a range from 1 to 100 nm in diameter.

[0015]

[Embodiments of the Invention]

While the organic polymer in the present invention refers to thermoplastic polymers such as polyester, polyamide and polyolefin, thermosetting polymers such as phenol resin and bio-polymers such as DNA, thermoplastic polymers are preferably used for the reason of moldability. Among these, polymers manufactured through polycondensation typified by polyester and polyamide are often characterized by high melting point and are more preferably used. The polymer may include particles, flame retarding agent, antistatic agent or the like added thereto. The polymer may also be copolymerized with other component to such an extent that the property of the polymer is not compromised.

According to the present invention, it is important to form the islands-in-sea structure consisting of two kinds of organic polymers which have different levels of solubility. The term "solubility" refers to the difference in the solubility to a solvent. The solvent may be an alkaline solution, an acidic solution, an organic solvent or a

supercritical liquid.

[0016]

Also according to the present invention, in order to make it easier to remove the sea component polymer with a solvent, it is important to use the low solubility polymer for the island component and use the high solubility polymer for the sea component. By using a polymer that is highly soluble to an alkaline solution as the high solubility polymer, it is made unnecessary to install an explosion-proof equipment in the dissolution facility, and is preferable in view of cost reduction and wider applications. The polymer that is highly soluble to an alkaline solution may be polyester, polycarbonate or the like, while copolymerized PET is particularly preferable. It is also preferable to use a polymer that is soluble to hot water as the high solubility polymer, since it relieves the load of waste liquid treatment. As the polymer that is soluble to hot water, polyalkylene glycol, polyvinyl alcohol or a derivative thereof, copolymerized polyester having a large content of sodium-5-sulfoisophthalic acid or the like is used. Particularly preferable is a polymer that has improved heat resistance by elongating the molecular chain through ester bond of polyalkylene glycol or PET made by copolymerizing 10 mol% or more of sodium-5-sulfoisophthalic acid.

[0017]

In consideration of the ease of processing the polymer alloy fiber to form a yarn, knitting or weaving and high level processing, it is preferable that the polymer that constitutes the sea component has a melting point, Vicat softening temperature or a thermal deformation temperature of 160°C or higher.

[0018]

For the polymer that constitutes the island component, the melting point is preferably 165°C or higher since it results in high heat resistance of the resultant nanofiber.

[0019]

Based on the above discussion, the following may be regarded as preferable combinations of polymers according to the present invention: Sea component polymer/island component polymer (solvent) = low-melting point polyester/nylon (aqueous alkali solution), polymer soluble to hot water/nylon (hot water), polymer soluble to hot water/polyester (hot water) and polymer soluble to hot water/polyolefin (hot water),

[0020]

According to the present invention, number average and spread of diameters of the island domains in the polymer alloy fiber are important factors for the purpose of making nanofibers having spread of single fiber fineness values. These parameters can be evaluated by observing a cross

section of the polymer alloy fiber under a transmission electron microscope (TEM), and measuring the diameters of 300 or more island domains that are randomly sampled in the same cross section. This measurement is made in at least five places, so as to measure the diameters of 1500 or more island domains in all. Positions to make these measurements are preferably separated by a distance of 10 m or more from each other in the longitudinal direction of the yarn.

[0021]

The number average of diameters is the simple mean of the diameters of the island domains that have been measured. It is important that the number average of diameters of the island domains is in a range from 1 to 100 nm. This is as thin as 1/100 to 1/1000 times that of the ultrafine fiber made from the conventional islands-in-sea multi-component fiber, in terms of single yarn diameter, and makes it possible to obtain a cloth for clothing applications that has an excellent feeling which can never been achieved with the ultrafine yarns of the prior art or a texturing cloth that can polish a hard disk to a level of smoothness which can never been achieved in the prior art. The number average of diameters of the island domains is preferably from 40 to 80 nm.

[0022]

The spread of the diameters of the island domains is



evaluated as described below. The area  $S_1$  of each island domain is totaled to obtain the total area ( $S_1 + S_2 + \dots + S_n$ ). Product of the area of the frequency (number) of the same area  $S$  and the frequency is divided by the total area, to give the value of area ratio of the island domains having the area  $S$ . For example, in case there are 350 island domains that have a diameter of 60 nm and the total area is  $3.64 \times 10^6 \text{ nm}^2$ , then the area ratio becomes  $(3.14 \times 30 \text{ nm} \times 30 \text{ nm} \times 350) / (3.64 \times 10^6 \text{ nm}^2) \times 100\% = 27.2\%$ . The area ratio corresponds to the volume ratio of the island domains of each size to the entire island components included in the polymer alloy fiber. The island domain component that has a large value of area ratio has greater contribution to the property of the nanofiber that is formed. It is important for the island domains included in the polymer alloy fiber of the present invention, that 60%, in area ratio, or more of the island domains are in a range from 1 to 100 nm in diameter of the island domains. This means that the nanofibers having such a level of fineness can be made that can never been achieved in the prior art, as most of the single fibers are 100 nm or smaller in diameter of the island domains. This makes it possible to make full use of the performance of the nanofiber, improve the stability of the quality of the fibrous article and, when used as a texturing cloth for texturing the hard disk surface, the small spread of fineness

values makes it possible to support abrasive particles evenly on the texturing cloth, thus resulting in a great improvement in the surface roughness of the hard disk surface. The area ratio of the island domains that are in a range from 1 to 100 nm in diameter is preferably 75% or more, more preferably 90%, further more preferably 95% or more and most preferably 98% or more.

[0023]

Similarly, it is preferable that a portion, where the area ratio of the island domains is higher, is concentrated in a component where diameter of the island domain is smaller. It is preferable that 60%, in area ratio, or more of the island domains are in a range from 1 to 80 nm in diameter, and it is more preferable that 75%, in area ratio, or more of the island domains are in a range from 1 to 80 nm in diameter.

[0024]

Another measure of the spread of diameters of the island domains is the area ratio of island domains that are in a section having a width of 30 nm in diameter of island domains. This is a parameter that corresponds to the half value width of the frequency distribution, or the degree of concentration of the values to a region around the median value. This means that the higher the area ratio in the section, the smaller the spread becomes. According to the present invention, area ratio of the island domains that are

in the section having a width of 30 nm is preferably 60% or more, more preferably 70% or more, and further more preferably 75% or more.

[0025]

While it has been described that the sizes and spread thereof of the island domains in the cross section of the polymer alloy fiber are important factors, it is also preferable that thick-fine unevenness in the longitudinal direction of the yarn is smaller, in order to ensure the stability of quality of the fibrous article that is made of the nanofibers. In case the nanofibers are used in a texturing cloth, for example, thick-fine unevenness in the longitudinal direction of yarn often has a significant influence on the size and number of scratches (blemishes on the surface of the textured article). Accordingly, it is preferable to control the Uster unevenness of the polymer alloy fiber of the present invention to 15% or less, more preferably to 5% or less and most preferably to 3% or less.

[0026]

It is preferable that the polymer alloy fiber of the present invention has a strength of 2.5 cN/dtex or higher and an elongation of 25% or higher, in order to minimize troubles such as the occurrence of fuzzing and yarn breakage in the process of crimping twisting, knitting, weaving or the like. Strength is more preferably 3 cN/dtex or higher. It is

preferable that the polymer alloy fiber has boiling water shrinkage of 25% or less, which suppresses the dimensional change of the cloth during dissolving of the sea component.

[0027]

While there is no restriction on the method for manufacturing the polymer alloy fiber of the present invention, a method described below, for example, may be employed.

[0028]

Two or more kinds of polymer having different levels of solubility to a solvent are alloyed, so as to form a molten polymer alloy that is spun and is cooled to solidify, thereby forming fibers. The fibers are subjected to drawing and heat treatment as required, thereby to obtain polymer alloy fibers. Since diameter of the nanofiber is substantially affected by the state of dispersion of the island size, it is very important to carry out high level of mixing and kneading by means of an extrusion kneader or a static mixer. In the case of the simple chip blending (Patent Document 2), the materials are not sufficiently mixed and kneaded and therefore it is difficult to disperse the islands of several tens of nanometers as in the present invention.

[0029]

While the specifics of the mixing and kneading process depend on the combination of the polymers, it is preferable

to carry out mixing and kneading using a twin-screw extrusion-kneader or, when a static mixer is employed, it is operated with a number of splits of  $100 \times 10^4$  or more.

[0030]

The combination of polymers is an important factor in order to disperse the islands-part polymer on the order of several tens of nanometers.

[0031]

In order to form the island domains (section of nanofiber) having cross sections as near to circle as possible, the island component and the sea component are preferably incompatible to each other. However, it is difficult to disperse the nanometer-sized islands by simply using a combination of mutually incompatible polymers. Thus it is preferable to optimize the compatibility of the polymers to be combined, which can be indicated by the solubility parameter (SP value). The SP value is a parameter that represents the cohesion force of a material and is defined as  $(\text{vaporizing energy/molar volume})^{1/2}$ . Materials having proximate values of SP are likely to make a polymer alloy of good compatibility. SP values of various polymers have been known, of which data are given in, for example, "Plastic Data Book", coedited by Asahi Kasei AMIDAS Co., Ltd. and the editorial staff of the Plastics, p189. It is preferable that the difference in the SP value between two

polymers is in a range from 1 to 9  $(\text{MJ}/\text{m}^3)^{1/2}$ , which makes it easier both to form a circular cross section of the island domain and achieve the dispersion of nanometer-sized islands through the use of incompatible polymers. A preferable example of combination is N6 and PET, of which SP values have a difference of about 6  $(\text{MJ}/\text{m}^3)^{1/2}$ . An example of combination that is not preferable is N6 and PE of which SP values have a difference of about 11  $(\text{MJ}/\text{m}^3)^{1/2}$ .

[0032]

In order to mix and knead with a high efficiency, it is preferable that melting points of the island component polymer and the sea component polymer have a difference not larger than  $20^\circ\text{C}$ , in which case there occurs no significant difference in the melting of the polymers, particularly in the case of using an extrusion kneader. While a polymer that is susceptible to thermal decomposition and/or thermal degradation is used as one of the polymers, it is necessary to control the mixing temperature and the spinning temperature to low levels. The use of polymers having smaller difference in the melting point is advantageous also for solving this problem. In the case of amorphous polymer which does not have a melting point, Vicat softening temperature or thermal deformation temperature is used instead of the melting point.

[0033]

The melt viscosity is also an important factor. The island component tends to disperse on the order of nanometers due to a higher tendency of the island component to deform under a shear force, when the polymer that makes the island component has a lower melt viscosity. However, an excessively low viscosity may turn the island component into sea component, making it difficult to achieve a high blend ratio of the island polymer to the entire fiber. Therefore, it is preferable that the melt viscosity of the polymer that makes the island component is 1/10 times or more of the melt viscosity of the polymer that makes the sea component.

[0034]

Since the island component and the sea component are incompatible to each other in the polymer alloy, the island components become more thermodynamically stable when cohered. However, in order to forcibly disperse the polymer as nano-sized islands, the polymer alloy has more polymer interfaces that are more unstable than a conventional polymer blend having larger dispersion sizes. As a result, when this polymer alloy is simply spun, the existence of a number of unstable polymer interfaces leads to such problems as "Barus phenomenon" in which the polymer flow swells immediately after the polymer is discharged through the spinneret, and insufficient stringiness due to destabilization of the polymer alloy surface. This not only causes excessive thick-

thin unevenness of the yarn but also makes it impossible to spin (negative effect of nano-sized polymer dispersion). In order to avoid such problems, it is preferable to control the shear stress between the spinneret orifice wall and the polymer being discharged through the spinneret to a low level. The shear stress between the spinneret orifice wall and the polymer is calculated by Hagen-Poiseuille's law that dictates that the shear stress (dyne/cm<sup>2</sup>) is given as  $R \times P/2L$ , where  $R$  is the radius of the spinneret orifice (cm),  $P$  is the pressure loss at the spinneret orifice (dyne/cm<sup>2</sup>) and  $L$  is the length of the spinneret orifice (cm). Pressure loss is calculated as  $P = 8 L \eta Q / \pi R^4$ , where  $\eta$  is the viscosity of the polymer (poise),  $Q$  is the discharge flow rate (cm<sup>3</sup>/sec) and  $\pi$  is the circular constant. In the melt spinning of the ordinary polyester, for example, while the shear stress between the spinneret orifice wall and the polymer is  $5 \times 10^6$  dyne/cm<sup>2</sup> or higher, it is preferable to control the shear stress to  $2 \times 10^6$  dyne/cm<sup>2</sup> or less in the case of melt spinning of polymer alloy as in the present invention. For this reason, there is a tendency to make the spinneret larger in orifice diameter and shorter in orifice length. However, when the diameter is increased and/or the length is decreased excessively, weighability of the polymer at the spinneret orifice decreases while fineness unevenness and spinnability become worse. Therefore, it is preferable to use such a



spinneret that has a polymer weighing section having an orifice provided above the spinneret orifice. Position of the polymer weighing section is preferably where the orifice diameter is reduced to be smaller than the discharge orifice.

[0035]

In order to ensure the stringiness and stability of spinning at sufficient levels during melt spinning, it is preferable to keep the surface temperature of the spinneret to 25°C or more higher than the melting point of the sea component.

[0036]

As described above, while it is important to properly design the spinneret for spinning the polymer alloy having dispersed constitution of nanometer sizes used in the present invention, it is also important to properly set the yarn cooling conditions. Since the polymer alloy is very unstable molten fluid as described above, it is preferably cooled and solidified immediately after being discharged from the spinneret. For this reason, distance between the bottom of the spinneret and the point where cooling begins is preferably in a range from 1 to 15 cm. The point where cooling begins is the position where positive cooling of the yarn begins, and it is assumed to be at the top end of the cooling equipment in an actual melt spinning machine.

[0037]

While there is no limitation on the spinning rate, the spinning rate is preferably as high as possible, in order to achieve a high draft during the spinning process. The draft is preferably 100 or higher, in order to obtain polymer alloy fibers having island domain of smaller diameter.

[0038]

The polymer alloy fiber that has been spun is preferably subjected to drawing and heat treatment processes. Preheating temperature during drawing is preferably set not lower than the glass transition temperature ( $T_g$ ) of the polymer that constitutes the island component for suppressing the occurrence of yarn unevenness. The polymer alloy fiber of the present invention can be processed at will such as crimping, yarn mixing or twisting.

[0039]

The manufacturing method of the present invention makes it possible to obtain polymer alloy fibers where the island component of several tens of nanometers is dispersed and yarn unevenness in the longitudinal direction is very small, by optimizing the combination of the polymers, the spinning condition and the drawing condition as described above.

[0040]

The polymer alloy fiber of the present invention obtained as described above is preferably used as the precursor for nanofiber. For example, a fibrous article

constituted from nanofibers can be easily made by forming the polymer alloy fibers into a fibrous article such as textile, knitting, nonwoven fabric or wad, and then removing the sea component polymer therefrom by means of a solvent. In this process, it is preferable to use a water-soluble solvent in order to reduce the equipment cost such as installing an explosion-proof equipment, use general-purpose facilities and mitigate the load on the environment. Specifically, an aqueous alkaline solution or hot water is preferably used as the solvent. Accordingly, the high solubility polymer is preferably a polymer such as polyester that is hydrolyzed by alkali, or a polymer that is soluble to hot water such as polyalkylene glycol, polyvinyl alcohol or a derivative thereof.

[0041]

With the manufacturing method described above, the aggregate of nanofibers is obtained having a morphology like spun yarn, each yarn comprising numerous nanofibers by the number of several thousands or several tens of thousands per cross section, the nanofibers having length of several tens of micrometers, or may sometimes be on the order of centimeter which are bonded or entangled with each other from point to point.

[0042]

With the manufacturing method described above,

particularly in case the static mixer is installed right above the spinneret, the aggregate of nanofibers having a morphology like filament yarn comprising nanofibers which may be infinitely long in theory.

[0043]

The aggregate of nanofibers obtained by the manufacturing method described above may have a morphology like filament-yarn or a morphology like spun yarn, where a plurality of nanofibers are oriented one-dimensionally and continue over a definite length.

[0044]

The aggregate of nanofibers of the present invention, because of the single fiber diameter as small as 1/10 to 1/100 that of the ultrafine fiber of the prior art, has dramatically increased the specific surface area. As a result, it demonstrates properties characteristic of the nanofiber which the conventional ultrafine fibers did not show.

[0045]

For example, the aggregate of nanofibers shows greatly improved adsorbing capability. In a comparison of water vapor adsorbing capability, namely moisture adsorbing capability between the aggregate of polyamide nanofibers of the present invention and the conventional ultrafine polyamide yarn, the aggregate of polyamide nanofibers of the

present invention showed the ratio of moisture adsorption as high as 6% while the conventional ultrafine polyamide yarn has the ratio of moisture adsorption of about 2%. Moisture adsorption capability is a very important property for clothing articles, in order to provide comfort of wear. It needs not to say that the polyamide nanofibers of the present invention has high capability of adsorbing harmful substances such as chlorine, trihalomethane, endocrine disruptors or compounds of heavy metals, in addition to water vapor. In addition, it has high releasing capability of aromatic substance or other useful substances.

[0046]

Moreover, since the aggregate of nanofibers obtained by the present invention has numerous voids that measure several nanometers to several hundreds of nanometers between the single nanofibers, the aggregate of nanofibers may demonstrate a unique property such as that of an ultra-porous material.

[0047]

The aggregate of nanofibers obtained by the present invention not only has high water-impregnating capability and high water holding capacity, but also may demonstrate such peculiar properties as follows. For example, while the conventional polyamide ultrafine fibers show a rate of elongation at absorbing water of about 3% in the longitudinal

direction of yarn, the aggregate of polyamide nanofibers of the present invention can show a rate of elongation at absorbing water as high as 7%. Moreover, the aggregate of nanofibers returns to the original length when dried after the elongation at absorbing water, the change in size is reversible. The reversible elongation in the longitudinal direction of yarn upon absorbing water/drying is an important property in view of soil releasing capability of cloth. According to the present invention, the ratio of elongation is preferably 5% or higher. The soil releasing capability refers to the capability of the cloth to get rid of stain when laundered. Since the aggregate of nanofibers elongates in the longitudinal direction of yarn upon absorbing water with the voids between the fibers (space between the fibers) in the woven fabric or the knitted fabric being expanded, stain sticking to the fibers can be easily removed.

[0048]

The aggregate of nanofibers of the present invention, when used in clothing applications, can produce fibrous articles having excellent hands such as sleekness of silk or dry feeling of rayon. Furthermore, fibrous articles that have ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized can be provided by separating the nanofibers from the aggregate of nanofibers by buffing or other process. In some cases, the

aggregate of nanofibers may show peculiar adhesiveness by absorbing a liquid such as water.

[0049]

It is preferable that the aggregate of nanofibers of the present invention has a strength of 1 cN/dtex or higher which enables it to improve the mechanical properties of the fibrous articles. Strength of the aggregate of nanofibers is more preferably 2 cN/dtex or higher.

[0050]

The aggregate of nanofibers obtained by the present invention may be used in a variety of product forms such as long fiber, short fiber, unwoven fabric, or thermally molded articles, unlike the conventional ones. The aggregate of nanofibers of the present invention may be used, not only in clothing applications such as shirts, blousons, pants or trousers, and coats, but also in wide applications including clothing materials such as cups and pads, interior applications such as curtains, carpets, mats as well as furniture, vehicle interior materials, industrial materials such as wiping cloth, texturing cloth or filters, environment-related applications such as water purifier or toxic substance removing apparatus and medical supplies such as cell adsorbing material. The peculiar adhesiveness can also be used in such applications as binder, medical field, living wares and the like. Moreover, the nanofibers obtained

by the present invention may be coated with various materials so as to provide functions such as moisture absorption, water repellent, flame retardation and electrical insulation, or can be used to produce novel composite materials by forming organic and inorganic polymers by using the nanofibers as the mold.

[0051]

The polymer alloy fiber of the present invention can be used not only as the precursor for the nanofiber as described above, but also as a polymer alloy material without making nanofibers.

[0052]

[Examples]

Now the present invention will be described in detail by way of example. The physical properties in the examples were determined by the following methods.

[0053]

A. Melt Viscosity of Polymer:

The melt viscosity of a sample polymer was determined using Capillograph 1B available from Toyo Seiki Seisaku-Sho, Ltd. The residence time of the sample polymer from charging of the sample to the beginning of determination was set at 10 minutes.

[0054]

B. Melting Point:



The melting point was defined as the peak top temperature at which a sample polymer melted in a second run as determined using Perkin Elmer DSC-7 at a temperature scanning rate of 16°C per minute, with an amount of the sample of 10 mg.

[0055]

#### C. Shear stress at the spinneret orifice

The shear stress between the spinneret orifice wall and the polymer was calculated by Hagen-Poiseuille's law that dictates that the shear stress (dyne/cm<sup>2</sup>) is given as  $R \times P/2L$ , where R is the radius of the spinneret orifice (cm), P is the pressure loss at the discharge orifice of the spinneret (dyne/cm<sup>2</sup>) and L is the length of the spinneret orifice (cm). Pressure loss is calculated as  $P = 8 L \eta Q / \pi R^4$ , where  $\eta$  is the viscosity of the polymer (poise), Q is the discharge flow rate (cm<sup>3</sup>/sec) and  $\pi$  is the circular constant. The value of polymer viscosity under the conditions of temperature and shear rate of the spinneret orifice is used.

[0056]

#### D. Uster Unevenness (U%) of Polymer Alloy Fiber:

The Uster unevenness was determined using USTER TESTER 4 available from Zellweger Uster in a normal mode at a yarn feed speed of 200 meters per minute.

[0057]

#### E. TEM Observation of Cross Section of Fiber:

Ultra-thin peaces of a sample fiber in a cross-sectional direction were prepared, and the cross sections of the fiber were observed using a transmission electron microscope (TEM). Metal staining was applied as required.

[0058]

TEM device: Model H-7100FA available from Hitachi, Ltd.

#### F. Number-average of Diameters of Island Domains

The number average of island domains is determined in the following manner. The diameters of the island domains in terms of equivalent circle were determined from TEM photographs of the cross section of the fiber using the image processing software (WINROOF), and the values were averaged. Diameters of 300 or more island domains that were randomly sampled in the same cross section were measured. This measurement was made at five points separated by a distance of 10 m or more from each other in the longitudinal direction of the polymer alloy yarn, so as to measure the diameters of 1500 or more island domains in all.

[0059]

#### G. Spread of Diameters of Island Domains

Spread of diameters of the island domains is determined in the following manner. By using the data used in determining the number average diameter described above, cross sectional area  $S_i$  of each island component is totaled to obtain the total area ( $S_1 + S_2 + \dots + S_n$ ). Product of the

frequency (number) of the island domains having the same diameter (area) and the area is divided by the total fineness ratio, to give the area ratio of the island domain.

[0060]

#### H. Spread of Diameters of Island Domains

Spread of diameters of the island domains is determined in the following manner. The area ratio of the island domains that fall within a zone of 30 nm in the single fiber diameter near the median of the number average of diameters of the island domains or in the portion of high area ratio is determined. This value of spread is also determined by using the data that were used to determine the single fiber diameter by number average. The ranges of diameters shown in Tables 2, 5, 8 and 11 of Examples represent a section having width of 30 nm in diameters of single yarns. For example, a section from 55 to 84 nm means a section of single yarn diameters not smaller than 55 nm and not larger than 84 nm. The area ratio represents the area ratio of the island domains that fall in the section of diameters.

[0061]

#### I. SEM Observation

Side surface of the fiber coated with platinum-palladium alloy by vapor deposition was observed under a scanning electron microscope.

[0062]

SEM device: Model S-4000 available from Hitachi, Ltd.

#### J. Mechanical Properties

Weight of 10 m segment of the aggregate of nanofibers was measured for five segments, and mean value thereof was used to determine the fineness (dtex) of the aggregate of nanofibers. Then at the room temperature (25°C), load-elongation curve was determined under the conditions specified in JIS L1013 with the initial sample length of 200 mm and drawing speed of 200 mm per minute. Then the load at rupture was divided by the initial fineness to give the strength. Elongation at break was divided by the initial sample length to give the elongation ratio, and accordingly the strength-elongation curve was determined.

[0063]

#### K. Ratio of Moisture Adsorption ( $\Delta MR$ ):

About 1 to 2 g of a sample is weighed in a weighing bottle, dried at 110°C for 2 hours, and the weight of the dried sample ( $W_0$ ) is determined. Next, the sample substance is held at 20°C with relative humidity of 65% for 24 hours, and its weight is then measured ( $W_{65}$ ), and the sample substance is then held at 30°C with relative humidity of 90% for 24 hours, and its weight is then measured ( $W_{90}$ ). The ratio of moisture adsorption  $\Delta MR$  is calculated according to the following equations.

[0064]

$$MR65 = [(W65 - W0)/W0] \times 100\% \quad (1)$$

$$MR90 = [(W90 - W0)/W0] \times 100\% \quad (2)$$

$$\Delta MR = MR90 - MR65 \quad (3)$$

L. Reversible Elongation at Absorbing Water and  
Percentage of Elongation in Longitudinal Direction of Yarn:

The original length (L0) of a sample fiber is determined after drying the fiber at 60°C for 4 hours. The fiber is immersed in water at 25°C for 10 minutes and is taken out of the water, and the length of the fiber after treatment (L1) is determined immediately thereafter. The length of the fiber after drying (L2) is then determined after drying the fiber at 60°C for 4 hours. The procedure of drying and immersion in water is repeated a total of three times. The sample is evaluated to have reversible elongation at absorbing water when it shows a percentage of elongation in the longitudinal direction of the yarn in the third procedure of 50% or more of that in the first procedure. The percentage of elongation in a longitudinal direction of the yarn is determined by calculation according to the following equation. The length of the fiber is determined by binding the sample fiber with two colored yarns at an interval of about 100 mm, and measuring the length between the two yarns.

[0065]

Percentage of elongation (%) in longitudinal direction  
of the yarn =  $((L1 - L0)/L0) \times 100(\%)$

## Example 1

A N6 (20% by weight) and a copolymerized PET (80% by weight) were melted and kneaded in a twin-screw extrusion-kneader at 260°C to obtain polymer alloy chips. The N6 had a melt viscosity of 530 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 220°C. The copolymerized PET had a melt viscosity of 3100 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 225°C, had been copolymerized with 8 mol% of isophthalic acid having a melting point of 235°C and 4 mol% of bisphenol A. The polymer alloy chips were melted in a melting section 2 at 275°C and were introduced to a spin block 3 at a spinning temperature of 280°C. The molten polymer alloy was filtrated through a metallic nonwoven fabric having a max hole diameter of 15 µm and was subjected to melt spinning through a spinneret 5 of which surface temperature was set to 262°C (FIG. 12). The spinneret had a weighing section 12, 0.3 mm in diameter, located above a discharge orifice, with orifice diameter 14 of 0.7 mm and orifice length 13 of 1.75 mm, as shown in FIG. 13. Discharge rate per orifice was set to 1.0 g per minute. The shear stress between the spinneret orifice and the polymer was sufficiently low at  $5.8 \times 10^5$  dyne/cm<sup>2</sup> (viscosity of the polymer alloy was 1400 poise at 262°C and shear rate was 416 sec<sup>-1</sup>). The distance from the bottom surface of the spinneret to the cooling start point (top end

of the cooling equipment 6) was 9 cm. The discharged thread was cooled and solidified by a cooling air at 20°C over a distance of one meter, fed with an oil by a finishing guide 8 arranged 1.8 meter down the spinneret 5 and was wound through a first take-up roller 9 and a second take-up roller 10, that were not heated, at a rate of 900 meters per minute. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The alloy fibers were subjected to heat drawing treatment with a first hot roller 17 at a temperature of 90°C and a second hot roller 18 at a temperature of 130°C (FIG. 14). Drawing ratio between the first hot roller 17 and the second hot roller 18 was set to 3.2. The polymer alloy fibers thus obtained showed good properties of 120 dtex, 36-filament, 4.0 cN/dtex in strength, 35% in elongation and U% = 1.7%. Observation of a cross section of the polymer alloy fiber under a TEM showed an islands-in-sea structure where the copolymerized PET (light portion) formed the sea and the N6 (dark portion) formed the islands (FIG. 1). The diameter of the N6 island domain by number average was 53 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber. Histograms of diameters of the N6 island domain by number average determined by analyzing the TEM micrograph are shown in FIG. 2 (diameter vs. frequency) and FIG. 3 (diameter vs. area ratio). The number

of island domains and the area ratio were determined for each class of 10 nm section in diameter. 10 nm section in diameter means that, for example, a section of diameters from 45 to 54 nm is represented by diameter 50 nm and a section of diameters from 65 to 74 nm is represented by diameter 70 nm. Physical properties of the polymer alloy fibers are shown in Table 2.

[0066]

The polymer alloy fibers thus obtained were formed into a round braid that was immersed in a 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers by hydrolysis. The round braid comprising solely of N6 yarn showed a macroscopic appearance of continuous filament yarn or spun yarn and maintained the form of round braid, despite the fact that the copolymerized PET constituting the sea component was removed. Moreover, quite unlike a round braid formed from an ordinary N6 fiber, this round braid did not show the slimy touch of nylon but showed the "sleekness" of silk or "dry feeling" of rayon.

[0067]

A yarn was drawn out of the round braid comprising solely of N6 yarn, and was observed on the side surface of the fiber under an optical microscope. The diameter of the fiber had been reduced to about two thirds that of the state



before alkali treatment, showing that the fiber shrank in the radial direction when the sea component was removed (FIG. 4). Then observation of the side surface of the fiber under an SEM showed that the yarn was not a single yarn, but an aggregate of nanofibers that was constituted from numerous coagulated nanofibers bonded to each other from point to point (FIG. 5). Spacing between the nanofibers in the N6 aggregate of nanofibers was from about several tens of nanometers to about 200 nm, with extremely small voids existing between the nanofibers. Picture of a cross section of the fiber under a TEM shown in FIG. 6 indicates that single fiber diameter of the N6 nanofiber is about several tens of nanometers. Analysis of the single fiber fineness of the N6 nanofibers and the spread thereof by the method employed in analyzing the island domain in the polymer alloy fiber showed that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm ( $3 \times 10^{-5}$  dtex). The fineness ratio of single fibers having single fiber fineness by number average was in a range from  $1 \times 10^{-7}$  to  $9 \times 10^{-5}$  dtex (equivalent to single fiber diameter from 1 to 100 nm) was 99%. Particularly, fineness ratio of single fibers having diameter in a range from 55 to 84 nm was 71%, with very small spread of single fiber fineness values. Fineness ratio was calculated from the diameters of the nanofibers, and corresponds to the area

ratio of the polymer alloy fibers. Diameters of the nanofibers are shown in Table 3.

[0068]

The measurement of the ratio of moisture adsorption ( $\Delta MR$ ) of the round braid consisting solely of the N6 showed a high moisture adsorbing capability of 6%, surpassing that of cotton. Further, a yarn comprising the aggregate of N6 nanofibers showed such a rate of elongation in the longitudinal direction of yarn at absorbing water, that indicated a reversible repetition of swelling upon absorbing water and shrinkage upon drying (FIG. 7). The rate of elongation in the longitudinal direction of yarn at absorbing water was 7%, far higher than 3% in the case of the ordinary N6 fiber. Measurement of mechanical properties of the yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%.

[0069]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0070]

As described above, use of the polymer alloy fibers of the present invention made it possible to obtain the aggregate of nanofibers unprecedented in the prior art and a

fibrous article constituted therefrom.

[0071]

#### Example 2

Polymer alloy chips were obtained using a twin-screw extrusion-kneader similarly to Example 1, except for using a N6 (20% by weight) having a melt viscosity of 2120 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and melting point of 220°C. The polymer chips were subjected to the melt spinning process similarly to Example 1, except for setting the discharge rate per orifice to 1.0 g per minute and shear stress between the spinneret orifice wall and the polymer at  $7.1 \times 10^5$  dyne/cm<sup>2</sup> (viscosity of the polymer alloy was 1700 poise at 262°C and at a shear rate of 416 sec<sup>-1</sup>). In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The undrawn yarn of the polymer alloy was drawn similarly to Example 1, except for setting the drawing ratio to 3.0, thereby to obtain polymer alloy fibers having good properties of 128 dtex, 36-filament, 4.1 cN/dtex in strength, 37% in elongation and U% = 1.2%. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 40 nm, indicating that

the N6 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 2.

[0072]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 43 nm ( $2 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 3.

[0073]

The yarn formed from the aggregate of N6 nanofibers showed a strength of 2.2 cN/dtex and elongation of 50%.

[0074]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0075]

### Example 3

Melt spinning operation was carried out similarly to Example 2, except for using a N6 (20% by weight) having a

melt viscosity of 5000 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and melting point of 220°C. The polymer chips were subjected to the melt spinning process similarly to Example 1, except for setting the shear stress between the spinneret orifice wall and the polymer at  $8.3 \times 10^5$  dyne/cm<sup>2</sup> (viscosity of the polymer alloy was 2000 poise at 262°C and at a shear rate of 416 sec<sup>-1</sup>), thereby to obtain undrawn polymer alloy yarn. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The undrawn yarn of the polymer alloy was drawn and annealed similarly to Example 2, thereby to obtain polymer alloy fibers having good properties of 128 dtex, 36-filament, 4.5 cN/dtex in strength, 37% in elongation and U% = 1.9%. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 60 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 2.

[0076]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained.

Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm ( $4 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 3.

[0077]

The yarn formed from the aggregate of N6 nanofibers showed a strength of 2.4 cN/dtex and elongation of 50%.

[0078]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0079]

#### Example 4

Melt spinning operation was carried out similarly to Example 3, except for setting the blending ratio of N6 to the polymer alloy as a whole at 50% by weight. The melt spinning process was conducted similarly to Example 1, except for setting the shear stress between the spinneret orifice wall and the polymer at  $1.5 \times 10^6$  dyne/cm<sup>2</sup>, thereby to obtain undrawn polymer alloy yarn. In this procedure, the fiber showed good spinnability and there occurred no fiber breakage during 24 hours of continuous spinning operation. The

undrawn yarn of the polymer alloy was drawn similarly to Example 2, thereby to obtain polymer alloy fibers having good properties of 128 dtex, 36-filament, 4.3 cN/dtex in strength, 37% in elongation and  $U\% = 2.5\%$ . Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 80 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber.

[0080]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers of morphology like spun yarn was obtained. The nanofibers were dried at 140°C under a stress. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 84 nm ( $6 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values.

[0081]

The yarn formed from the aggregate of N6 nanofibers showed a strength of 2.6 cN/dtex and elongation of 50%.

[0082]

Comparative Example 1

An islands-in-sea composite yarn was made according to a method described in Example 1 of Japanese Unexamined Patent Publication No. 53-106872, using a PET having a melt viscosity of 1800 poise ( $290^{\circ}\text{C}$  at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of  $255^{\circ}\text{C}$  as the island component, and a polystyrene (PS) having a melt viscosity of 1000 poise ( $290^{\circ}\text{C}$  at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a Vicat softening temperature of  $107^{\circ}\text{C}$  as the sea component. The island domains had a large diameter by number average of  $2.0 \mu\text{m}$ . This yarn was treated with trichloroethylene so as to remove 99% or more of the PS according to a method described in Example of Japanese Unexamined Patent Publication No. 53-106872, thereby to obtain an ultrafine yarn. TEM observation of a cross section of the ultrafine fiber showed a large single fiber diameter of  $2.0 \mu\text{m}$  ( $0.04 \text{ dtex}$ ).

[0083]

#### Comparative Example 2

A N6 having a melt viscosity of 500 poise ( $280^{\circ}\text{C}$  at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of  $220^{\circ}\text{C}$  and a PET having a melt viscosity of 2100 poise ( $280^{\circ}\text{C}$  at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of  $255^{\circ}\text{C}$  were blended in chips with the content of the N6 set to 20% by weight. Then melt spinning was carried out similarly to Example 1, except for melting at  $290^{\circ}\text{C}$ , setting the spinning temperature to  $296^{\circ}\text{C}$  and the surface temperature of the



spinneret to 280°C and using a straight spinneret having 36 orifices, an orifice diameter of 0.30 mm and an orifice length of 50 mm. An undrawn yarn was wound at a spinning rate of 1000 m/min. Because of the simple chip blending operation and a large difference in the melting point between the polymers, a significant blending unevenness of the N6 and the PET and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a small quantity of undrawn yarn was obtained and was drawn similarly to Example 1 with temperature of the first hot roller 17 set to 85°C and the drawing ratio set to 3 times, thereby to obtain a drawn yarn of 100 dtex and 36-filament. The island domains had a large diameter by number average of 1.0  $\mu\text{m}$ .

[0084]

This yarn was formed into a round braid similarly to Example 1, and was also subjected to alkali treatment to remove 99% or more of the PET component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 400 nm to 4  $\mu\text{m}$  (single fiber fineness from  $1 \times 10^{-3}$  to  $1 \times 10^{-1}$  dtex) was formed. However, it showed single fiber fineness by number average of a large value of  $9 \times 10^{-3}$  dtex (single fiber diameter of 1.0  $\mu\text{m}$ ). The N6 ultrafine yarn also showed a

large spread of single fiber fineness values.

[0085]

### Comparative Example 3

A N6 having a melt viscosity of 3950 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 220°C and a PE having a melt viscosity of 560 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 105°C were blended in chips with the content of the N6 being set to 65% by weight. Then after melting by using an apparatus shown in FIG. 15, the temperature of a single-screw extrusion kneader 21 being set at 260°C, melt spinning was carried out similarly to Example 1, except for using a straight spinneret having 12 orifices, an orifice diameter of 0.30 mm and an orifice length of 50 mm. A significant blending unevenness of the N6 and the PE and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a small quantity of undrawn yarn was obtained, and was subjected to drawing and heat treatment similarly to Example 1, thereby to obtain a drawn yarn of 82 dtex and 12-filament. The drawing ratio was set to 2.0. The island domains had a large diameter by number average of 1.0 μm.

[0086]

This yarn was formed into a round braid similarly to Example 1, and was subjected to dissolving treatment with

toluene at 85°C for one hour or more, thereby so as to remove 99% or more of the PE component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 500 nm to 3  $\mu\text{m}$  (single fiber fineness  $2 \times 10^{-3}$  to  $8 \times 10^{-2}$  dtex) was formed. However, it showed single fiber fineness by number average of a large value of  $9 \times 10^{-3}$  dtex (single fiber diameter of 1.0  $\mu\text{m}$ ). The N6 ultrafine yarn also showed a large spread of single fiber fineness values.

[0087]

#### Comparative Example 4

A melt spinning operation was carried out similarly to Comparative Example 3 using an apparatus shown in FIG. 17 wherein a N6 having a melt viscosity of 1500 poise (262°C at a shear rate of 121.6  $\text{sec}^{-1}$ ) and a melting point of 220°C and a PE having a melt viscosity of 1450 poise (262°C at a shear rate of 121.6  $\text{sec}^{-1}$ ) and a melting point of 105°C were introduced into a twin-screw extrusion-kneader while weighing the polymers separately with the content of the N6 set to 20% by weight. A significant blending unevenness of the N6 and the PE and a significant Barus under the spinneret were observed. While the yarn could not be wound stably due to low stringiness, a small quantity of undrawn yarn was obtained and was drawn and subjected to heat treatment

similarly to Example 1, thereby to obtain a drawn yarn of 82 dtex and 12-filament. The drawing ratio was set to 2.0. The island domains had a large diameter by number average of 374 nm. Spread of the island domain diameters showed a large value as shown in FIG. 8 and FIG. 9.

[0088]

This yarn was formed into a round braid similarly to Example 1, and was subjected to dissolving treatment with toluene at 85°C for one hour or more, thereby to remove 99% or more of the PE component. A yarn comprising solely of N6 was drawn out of the round braid. TEM observation of a cross section of the fiber showed that an ultrafine yarn having single fiber diameter of 100 nm to 1  $\mu$ m (single fiber fineness  $9 \times 10^{-5}$  to  $9 \times 10^{-3}$  dtex) was formed. However, it showed single fiber fineness by number average of a large value of  $1 \times 10^{-3}$  dtex (single fiber diameter of 384 nm).

[0089]

#### Comparative Example 5

An islands-in-sea composite yarn was made according to a method described in Comparative Example 1 of Japanese Examined Patent Publication No. 60-28922, using a spinning pack and a spinneret shown in FIG. 11 of the aforementioned Publication and using a PS and a PET described in Comparative Example 1 of the Publication. A blended polymer of PS and PET in weight proportion of 2:1 was used as the island

component and PS was used as the sea component of the islands-in-sea composite yarn. The islands-in-sea proportion was 1:1 in a weight proportion. Specifically, PET was used as component A, and PS was used as components B and C in FIG. 11 of the aforementioned Publication. An observation of a cross section of the fiber showed the existence of a trace of island domains having diameter of about 100 nm at the minimum. However, since the PET was not dispersed satisfactorily in the PS, it showed a large diameter by number average of 316 nm. Spread of the island domain diameters showed large value as shown in FIG. 10 and FIG. 11. This yarn was treated with trichloroethylene similarly to Comparative Example 1 of the Publication described above, so as to remove 99% or more of the PS, thereby to obtain an ultrafine yarn. Observation of a cross section of the fiber showed the existence of a trace of single yarn having diameter of about 100 nm at the minimum, but showed single fiber fineness by number average of a large value of  $9 \times 10^{-4}$  dtex (single fiber diameter of 326 nm).

[0090]

[Table 1]

	Island polymer			Sea polymer			Shear stress at orifice (dyne/cm <sup>2</sup> )
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 1	N6	530	20	Copolymerized PET	3100	80	$5.8 \times 10^5$
Example 2	N6	2120	20	Copolymerized PET	3100	80	$7.1 \times 10^5$
Example 3	N6	5000	20	Copolymerized PET	3100	80	$8.3 \times 10^5$
Example 4	N6	5000	50	Copolymerized PET	3100	50	$1.5 \times 10^6$
Comparative Example 1	PET	1800	96	PS	1000	4	-
Comparative Example 2	N6	500	20	PET	2100	80	$4.1 \times 10^6$
Comparative Example 3	N6	3950	65	PE	560	35	$6.4 \times 10^6$
Comparative Example 4	N6	1500	20	PE	1450	80	$4.0 \times 10^6$
Comparative Example 5	PS/PET	-	50	PS	-	50	-

[Table 2]

	Number-average diameter of island domains (nm)	Spread of island domains		Strength (cN/dtex)	U% (%)
		Area ratio (%)	Range Range of diameters: Area ratio		
Example 1	53	100	45 - 74 nm: 72%	4.0	1.7
Example 2	40	100	35 - 64 nm: 75%	4.1	1.2
Example 3	60	99	55 - 84 nm: 70%	4.5	1.9
Example 4	80	85	65-94 nm: 66%	4.3	2.5
Comparative Example 1	2000	0	-	-	-
Comparative Example 2	1000	0	974 - 1005 nm: 10%	-	23.5
Comparative Example 3	1000	0	974 - 1005 nm: 10%	-	22.7
Comparative Example 4	374	0	395 - 424 nm: 10%	-	20.3
Comparative Example 5	316	0	395 - 424 nm: 10%	-	17.3

Area ratio: Area ratio of island domains having diameters in a range from 1 to 100 nm.

Range: Area ratio in a section 30 nm wide in diameters.

[0092]

[Table 3]

	Number-average of nanofibers		Spread of nanofibers		Strength of nanofibers (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range Range of diameters: Fineness ratio	
Example 1	56	$3 \times 10^{-5}$	99	55 - 84 nm: 71%	2.0
Example 2	43	$2 \times 10^{-5}$	100	45 - 74 nm: 75%	2.2
Example 3	65	$4 \times 10^{-5}$	98	65 - 94 nm: 70%	2.4
Example 4	84	$6 \times 10^{-5}$	78	75 - 104 nm: 64%	2.6
Comparative Example 1	2000	$4 \times 10^{-2}$	0	-	-
Comparative Example 2	1000	$9 \times 10^{-3}$	0	974 - 1005 nm: 10%	-
Comparative Example 3	1000	$9 \times 10^{-3}$	0	974 - 1005 nm: 10%	-
Comparative Example 4	384	$1 \times 10^{-3}$	0	395 - 424 nm: 10%	-
Comparative Example 5	326	$9 \times 10^{-4}$	0	395 - 424 nm: 10%	-

Fineness ratio: Fineness ratio of single fiber fineness in a range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  dtex

Range: Area ratio in a section 30 nm wide in diameters.



[0093]

Example 5

The N6 and the copolymerized PET used in Example 1 were separately melted at 270°C in an apparatus shown in FIG. 16, and the molten polymer was introduced into a spin block 3 having a spinning temperature of 280°C. The two polymers were carefully mixed through  $104 \times 10^4$  splits in a static mixer 22 ("Hi-Mixer", available from TORAY Engineering Co., Ltd.) installed in a spinning pack 4, and melt spinning operation was carried out similarly to Example 1. The polymer consisted of 20% by weight of the N6 and 80% by weight of the copolymerized PET. The undrawn yarn was drawn and subjected to annealing similarly to Example 1. Polymer alloy fibers thus obtained showed good properties of 120 dtex, 36-filament, 3.9 cN/dtex in strength, 38% in elongation and  $U\% = 1.7\%$ . Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 52 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 5.

[0094]

The polymer alloy fibers thus obtained were subjected

to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 54 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 6.

[0095]

The ratio of moisture adsorption ( $\Delta MR$ ) of a round braid formed from the aggregate of nanofibers was 5%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%.

[0096]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0097]

#### Example 6

The N6 and the copolymerized PET used in Example 1 were melted, mixed and kneaded in a twin-screw extrusion-kneader at 270°C using the apparatus shown in FIG. 17, and the molten polymer was introduced into a spin block 3 having a spinning temperature of 280°C, and was subjected to melt spinning

process similarly to Example 1. The polymer consisted of 20% by weight of the N6 and 80% by weight of the copolymerized PET. The undrawn yarn was drawn and subjected to annealing similarly to Example 1. Polymer alloy fibers thus obtained showed good properties of 120 dtex, 36-filament, 3.9 cN/dtex in strength, 38% in elongation and  $U\% = 1.7\%$ . Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands similarly to Example 1. The diameter of the N6 island domain by number average was 54 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 5.

[0098]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 6.

[0099]

The ratio of moisture adsorption ( $\Delta MR$ ) of a round braid

formed from the aggregate of nanofibers was 5%. A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 50%.

[0100]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0101]

[Table 4]

	Island polymer			Sea polymer			Order of kneading	Shear stress at orifice (dyne/cm <sup>2</sup> )
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)		
Example 5	N6	530	20	Copolymerized PET	3100	80	In the spinning pack	$5.8 \times 10^5$
Example 6	N6	530	20	Copolymerized PET	3100	80	Before the spinning pack	$5.8 \times 10^5$

[0102]

[Table 5]

	Number-average diameter of island domains (nm)	Spread of island domains		Strength (cN/dtex)	U% (%)
		Area ratio (%)	Range Range of diameters: Area ratio		
Example 5	52	100	45 - 74 nm: 72%	3.9	1.7
Example 6	54	100*	45 - 74 nm: 71%	3.9	1.7

90

Area ratio: Area ratio of island domains having diameters in a range from 1 to 100 nm.

Range: Area ratio in a section 30 nm wide in diameters.

[0103]

[Table 6]

	Number-average of nanofibers		Spread of nanofibers		Strength of nanofibers (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range Range of diameters: Fineness ratio	
Example 5	54	$3 \times 10^{-5}$	99	55 - 84 nm: 72%	2.0
Example 6	56	$3 \times 10^{-5}$	99	55 - 84 nm: 70%	2.0

Fineness ratio: Fineness ratio of single fiber fineness in a range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  dtex

Range: Area ratio in a section 30 nm wide in diameters.

[0104]

Example 7

Kneading and melt spinning operations were carried out similarly to Example 1, except for using "Paogen PP-15" (melt viscosity of 3500 poise at 262°C at a shear rate of 121.6 sec<sup>-1</sup>, melting point of 60°C) available from Daiichi Kogyo Seiyaku Co., Ltd., that is a polymer soluble to hot water, for the copolymerized PET and setting the spinning rate to 5000 m/min, where the shear stress between the spinneret orifice wall and the polymer was  $7.5 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers thus obtained showed good properties of 70 dtex, 36-filament, 3.8 cN/dtex in strength, 50% in elongation and U% = 1.7%. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the copolymerized PET formed the sea and the N6 formed the islands. The diameter of the N6 island domain by number average was 53 nm, indicating that the N6 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0105]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was

analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 56 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0106]

A yarn comprising the aggregate of N6 nanofibers showed a strength of 2.0 cN/dtex and an elongation of 60%.

[0107]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0108]

#### Example 8

By using a N66 having a melt viscosity of 1000 poise ( $280^{\circ}\text{C}$  at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of  $250^{\circ}\text{C}$  instead of the N6 and using an apparatus shown in FIG. 16, the N66 was melted at  $270^{\circ}\text{C}$  and the polymer soluble to hot water that was used in Example 7 was melted at  $80^{\circ}\text{C}$ . The molten polymers were introduced into the spin block 3 having a spinning temperature of  $280^{\circ}\text{C}$ . The two polymers were subjected to melt spinning operation similarly to Example 5. Proportions of the polymers were 20% by weight for the N66 and 80% by weight for the polymer soluble to hot water, and



discharge per orifice was set to 1.0 g per minute. Spinning rate was set to 5000 meters per minute, and the shear stress between the spinneret orifice wall and the polymer showed sufficiently low value of  $6.2 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 70 dtex, 36-filament, 4.5 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the N66 formed the islands. The diameter of the N66 island domain by number average was 58 nm, indicating that the N66 was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0109]

The polymer alloy fibers thus obtained were subjected to alkali treatment similarly to Example 1, and an aggregate of nanofibers having morphology like spun yarn was obtained. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 62 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0110]

A yarn comprising the aggregate of N6 nanofibers showed

a strength of 2.5 cN/dtex and an elongation of 60%.

[0111]

When the round braid was buffed, it showed excellent hands providing ultra-soft feeling like peach skin, or soft and moist touch like human skin which have never been realized by the ultrafine fibers of the prior art.

[0112]

#### Example 9

A copolymerized PET and a polymer soluble to hot water were mixed, kneaded and melt-spun similarly to Example 6, except for using the copolymerized PET (8% by weight of PEG 1000 and 7 mol% of isophthalic acid were copolymerized) having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 235°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the copolymerized PET and 80% by weight for the polymer soluble to hot water, and discharge per orifice was set to 1.0 g per minute. Spinning rate was set to 6000 meters per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $7.8 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 55% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to

hot water formed the sea and the copolymerized PET formed the islands. The diameter of the copolymerized PET island domain by number average was 52 nm, indicating that the copolymerized PET was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0113]

The polymer alloy fibers thus obtained were formed into a round braid similarly to Example 1, and was treated with hot water at 100°C so as to dissolve the polymer soluble to hot water. The round braid thus formed from the aggregate of nanofibers had sleekness of silk or dry feeling of rayon. Spread of single fiber fineness values of the nanofibers was analyzed similarly to Example 1, showing that the nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 54 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0114]

The ratio of moisture adsorption ( $\Delta MR$ ) of the round braid formed from the aggregate of nanofibers was 2%. A yarn comprising the aggregate of nanofibers of the N6 showed a strength of 1.5 cN/dtex and an elongation of 70%.

[0115]

Example 10

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a PET having a melt viscosity of 1900 poise (280°C, at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 255°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PET and 80% by weight for the polymer soluble to hot water. Melting temperature of the PET was set at 285°C, melting temperature of the polymer soluble to hot water was set at 80°C, and spinning temperature was set at 295°C and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $8.0 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PET formed the islands. The diameter of the PET island domain by number average was 62 nm, indicating that the PET was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0116]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers

thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm ( $3 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0117]

#### Example 11

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a PBT having a melt viscosity of 1200 poise (262°C at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of 225°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PET and 80% by weight for the polymer soluble to hot water. Melting temperature of the PBT was set at 255°C, melting temperature of the polymer soluble to hot water was set at 80°C, spinning temperature was 265°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $7.5 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PBT formed the islands. The diameter of the PBT island domain by

number average was 62 nm, indicating that the PBT was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0118]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm ( $4 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0119]

#### Example 12

Kneading and melt spinning operations were carried out similarly to Example 9, except for using polytrimethylene phthalate (PTT) having a melt viscosity of 2200 poise (262°C at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of 225°C, and using the polymer soluble to hot water that was used in Example 7. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $7.3 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 60 dtex, 36-filament, 3.0 cN/dtex in strength and 45% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where

the polymer soluble to hot water formed the sea and the PTT formed the islands. The diameter of the PTT island domain by number average was 62 nm, indicating that the PTT was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

#### [0120]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 65 nm ( $4 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

#### [0121]

#### Example 13

Kneading and melt spinning operations were carried out similarly to Example 9, except for using a poly-lactic acid (PLA) having a melt viscosity of 3500 poise (220°C at a rate of shear of  $121.6 \text{ sec}^{-1}$ ) and a melting point of 170°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PLA and 80% by weight for the polymer soluble to hot water. Spinning temperature was 235°C, surface temperature of the spinneret was 220°C, and discharge per orifice was set

to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $8.0 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 60 dtex, 36-filament, 2.5 cN/dtex in strength and 35% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PLA formed the islands. The diameter of the PLA island domain by number average was 48 nm, indicating that the PLA was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 8.

[0122]

An aggregate of nanofibers was formed in a process similar to that of Example 9 using the polymer alloy fibers thus obtained. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 50 nm ( $2 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 9.

[0123]



[Table 7]

	Island polymer			Sea polymer			Order of kneading
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 7	N6	530	20	Polymer soluble to hot water	3500	80	Chip blending
Example 8	N66	1000	20	Polymer soluble to hot water	2200	80	In the spinning pack
Example 9	Copolymerized PET	3000	20	Polymer soluble to hot water	3500	80	Before the spinning pack
Example 10	PET	1900	20	Polymer soluble to hot water	2200	80	In the spinning pack
Example 11	PBT	1200	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 12	PTT	2200	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 13	PLA	3500	20	Polymer soluble to hot water	6000	80	In the spinning pack

[Table 8]

	Number-average diameter of island domains (nm)	Spread of island domains		Strength (cN/dtex)	U% (%)
		Area ratio (%)	Range Range of diameters: Area ratio		
Example 7	53	100	45 - 74 nm: 72%	3.8	1.7
Example 8	58	100	55 - 84 nm: 70%	4.5	1.7
Example 9	52	100	45 - 74 nm: 72%	3.0	1.6
Example 10	62	97	55 - 84 nm: 65%	3.0	2.3
Example 11	62	98	55 - 84 nm: 68%	3.0	2.0
Example 12	62	98	55 - 84 nm: 65%	3.0	2.0
Example 13	48	100	45 - 74 nm: 75%	2.5	1.2

73

Area ratio: Area ratio of island domains having diameters in a range from 1 to 100 nm.

Range: Area ratio in a section 30 nm wide in diameters.

[0125]

[Table 9]

	Number-average of nanofibers		Spread of nanofibers		Strength of nanofibers (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range Range of diameters: Fineness ratio	
Example 7	56	$3 \times 10^{-5}$	99	55 - 84 nm: 72%	2.0
Example 8	62	$3 \times 10^{-5}$	98	55 - 84 nm: 68%	2.5
Example 9	54	$3 \times 10^{-5}$	99	55 - 84 nm: 71%	2.0
Example 10	65	$5 \times 10^{-5}$	98	55 - 84 nm: 65%	2.0
Example 11	65	$4 \times 10^{-5}$	98	55 - 84 nm: 65%	2.0
Example 12	65	$4 \times 10^{-5}$	98	55 - 84 nm: 65%	2.0
Example 13	50	$2 \times 10^{-4}$	100	45 - 74 nm: 72%	1.9

Fineness ratio: Fineness ratio of single fiber fineness in a range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  dtex

Range: Fineness ratio in a section 30 nm wide in diameters.

[0126]

Example 14

Kneading and melt spinning operations were carried out similarly to Example 8, except for using a polycarbonate (PC) having a melt viscosity of 3000 poise (262°C at a shear rate of 121.6 sec<sup>-1</sup>) and a thermal deformation temperature of 140°C, and using the polymer soluble to hot water that was used in Example 7. Proportions of the polymers were 20% by weight for the PC and 80% by weight for the polymer soluble to hot water. Discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $7.5 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 70 dtex, 36-filament, 2.2 cN/dtex in strength and 35% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PC formed the islands. The diameter of the PC island domain by number average was 85 nm, indicating that the PC was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 11.

[0127]

A round braid was formed in a process similar to that of Example 1 using the polymer alloy fibers thus obtained.

The round braid was treated in warm water of 40°C for 10 hours so as to dissolve 99% or more of the polymer soluble to hot water, thereby to obtain an aggregate of nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 88 nm ( $8 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 12.

[0128]

#### Example 15

Kneading and melt spinning operations were carried out similarly to Example 8, except for using polymethylpentene (PMP) having a melt viscosity of 3000 poise (262°C at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of 220°C and a PS having a melt viscosity of 3000 poise (262°C at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a Vicat softening temperature of 105°C, and setting the spinning speed to 1500 meters per minute. Then drawing and annealing operations were carried out similarly to Example 1 by setting the drawing ratio to 1.5. Proportions of the polymers were 20% by weight for the PMP and 80% by weight for the PS, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $7.5 \times 10^5 \text{ dyne/cm}^2$ . The polymer alloy fibers having 77 dtex, 36-filament, 3.0 cN/dtex in strength and 40% in elongation were obtained. Observation of a cross section of the polymer

alloy fiber under a TEM showed islands-in-sea structure where the PS formed the sea and the PMP formed the islands. The diameter of the PMP island domain by number average was 70 nm, indicating that the PMP was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 11.

[0129]

The polymer alloy fibers thus obtained were formed into a round braid similarly to Example 1, and was treated with concentrated hydrochloric acid at 40°C so as to embrittle the PS. Then the PS was removed by methyl ethyl ketone, thereby to obtain a round braid constituted from the aggregate of PMP nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 73 nm ( $5 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 12.

[0130]

#### Example 16

Kneading, melt spinning, drawing and annealing operations were carried out similarly to Example 15, except for using a PP having a melt viscosity of 3000 poise (220°C at a shear rate of  $121.6 \text{ sec}^{-1}$ ) and a melting point of 162°C and the polymer soluble to hot water used in Example 7. Proportions of the polymers were set to 20% by weight for the PP and 80% by weight for the polymer soluble to hot water.

Spinning temperature was set to 235°C, surface temperature of the spinneret was set to 220°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice and the polymer showed a sufficiently low value of  $6.5 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 77 dtex, 36-filament, 2.5 cN/dtex in strength and 50% in elongation were obtained. Observation of a cross section of the polymer alloy fiber under a TEM showed islands-in-sea structure where the polymer soluble to hot water formed the sea and the PP formed the islands. The diameter of the PP island domain by number average was 48 nm, indicating that the PP was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 11.

#### [0131]

The polymer alloy fibers thus obtained were formed into an aggregate of nanofibers in a process similar to Example 9. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 50 nm ( $2 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 12.

#### [0132]

##### Example 17

Kneading, melt spinning, drawing and annealing operations were carried out similarly to Example 15, except

for using a polyphenylene sulfide (PPS) having a melt viscosity of 2000 poise (300°C at a shear rate of 121.6 sec<sup>-1</sup>) and a melting point of 280°C and a N6 having a melt viscosity of 2000 poise (300°C at a shear rate of 121.6 sec<sup>-1</sup>). Proportions of the polymers were set to 20% by weight for the PPS and 80% by weight for the N6. Melting point of the PPS was set to 320°C, melting point of the N6 was set to 270°C, spinning temperature was set to 320°C, surface temperature of the spinneret was set to 300°C, and discharge per orifice was set to 1.0 g per minute. Shear stress between the spinneret orifice wall and the polymer showed a sufficiently low value of  $6.2 \times 10^5$  dyne/cm<sup>2</sup>. The polymer alloy fibers having 77 dtex, 36-filament, 5.2 cN/dtex in strength and 50% in elongation were obtained. Observation of a cross section of the polymer alloy fiber thus obtained under a TEM showed islands-in-sea structure where the N6 formed the sea and the PPS formed the islands. The diameter of the PPS island domain by number average was 65 nm, indicating that the PPS was dispersed on the nanometer order in the polymer alloy fiber. Physical properties of the polymer alloy fibers are shown in Table 11.

[0133]

A round braid was formed in a process similar to that of Example 1 using the polymer alloy fibers thus obtained. The round braid was treated with formic acid so as to



dissolve the N6, thereby to obtain a round braid constituted from an aggregate of PPS nanofibers. The nanofiber had such an unprecedented fineness as the single fiber diameter by number average was 68 nm ( $5 \times 10^{-5}$  dtex), with very small spread of single fiber fineness values. Diameters of the nanofibers are shown in Table 12.

[0134]

[Table 10]

	Island polymer			Sea polymer			Order of kneading
	Polymer	Melt viscosity (poise)	Proportion (% by weight)	Polymer	Melt viscosity (poise)	Proportion (% by weight)	
Example 14	PC	3000	20	Polymer soluble to hot water	3500	80	In the spinning pack
Example 15	PMP	3000	20	PS	3000	80	In the spinning pack
Example 16	PP	3000	20	Polymer soluble to hot water	6000	80	In the spinning pack
Example 17	PPS	2000	20	N6	2000	80	In the spinning pack

[0135]

[Table 11]

	Number-average diameter of island domains (nm)	Spread of island domains		Strength (cN/dtex)	U% (%)
		Area ratio (%)	Range of diameters: Area ratio		
Example 14	85	73	75 - 104 nm: 70%	2.2	5.1
Example 15	70	95	65 - 94 nm: 73%	3.0	2.0
Example 16	48	100	45 - 74 nm: 75%	2.5	2.0
Example 17	65	98	55 - 84 nm: 70%	5.2	2.0

81

Area ratio: Area ratio of island domains having diameters in a range from 1 to 100 nm.

Range: Area ratio in a section 30 nm wide in diameters.

[0136]

[Table 12]

	Number-average of nanofibers		Spread of nanofibers		Strength (cN/dtex)
	Diameter (nm)	Fineness (dtex)	Fineness ratio (%)	Range Range of diameters: Fineness ratio	
Example 14	88	$8 \times 10^{-5}$	70	85 - 114 nm: 70%	1.5
Example 15	73	$5 \times 10^{-5}$	94	65 - 94 nm: 72%	1.7
Example 16	50	$2 \times 10^{-5}$	100	45 - 74 nm: 72%	1.5
Example 17	68	$5 \times 10^{-5}$	92	65 - 94 nm: 68%	3.0

Fineness ratio: Fineness ratio of single fiber fineness in a range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  dtex

Range: Fineness ratio in a section 30 nm wide in diameters.

[0137]

Example 18

The polymer alloy fibers made in Examples 1 to 13 were woven into plain weaves. The weaves were scoured in hot water at 100°C (bath ratio 1:100) including a surfactant (GRANUP® manufactured by Sanyo Chemical Industries, Ltd.) and sodium carbonate each in concentration of 2 g per liter. Duration of scouring was set to 40 minutes for the weaves made from the yarns of Examples 1 to 6 (comprising sea component formed from copolymerized PET), and 90 minutes for the weaves made from the yarns of Examples 7 to 13 (comprising sea component formed from polymer soluble to hot water). In this process, 99% or more of the polymer soluble to hot water was removed. This was followed by an intermediate heat-setting at 140°C (intermediate heat-setting at 170°C only for the weave formed from the yarn of Example 10). The weaves made from the yarns of Examples 1 to 6 were subjected to alkali treatment by means of 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:100) for 90 minutes, thereby to remove 99% or more of the copolymerized PET, or the sea component. This was followed by final heat-setting at 140°C (final heat-setting at 170°C only for the weave formed from the yarn of Example 10). Cloths thus obtained were dyed by an ordinary method, and every one of the cloths made a beautifully dyed cloth without any dyeing unevenness.

The woven fabric made from the aggregate of nanofibers had excellent hands such as "dry feeling" of rayon. They also showed a high ratio of moisture adsorption ( $\Delta MR$ ) of 6% in the case of the woven fabric formed from the yarns of Examples 1 to 8, and 2% in the case of the woven fabric formed from the yarns of Example 9, both indicating the capability to produce comfortable clothes. Furthermore, when buffed, the woven fabric showed ultra-soft feeling like peach skin, or soft and moist touch like human skin which had never been realized with the conventional ultrafine fibers.

[0138]

#### Comparative Example 6

The N6-blended fibers made in Comparative Examples 2 to 4 were woven into plain weaves similarly to Example 18. Only poor woven fabrics with much fluff and low surface quality could be made because the yarn had thick-thin unevenness in the longitudinal direction of yarn and much fluff due to unstable spinning. These woven fabrics were scoured followed by intermediate heat-setting. The woven fabric formed from the yarn of Comparative Example 2 was subjected to alkali treatment similarly to Example 18 followed by the final heat-setting, and was dyed by the ordinary method. The woven fabric formed from the yarns of Comparative Examples 3 and 4 were immersed in toluene at 85°C for 60 minutes so as to remove 99% or more of the PE by dissolution. These woven

fabrics were subjected to the final heat-setting and were dyed by the ordinary method. The cloths thus obtained had poor quality with much dyeing unevenness and fluff. Hands of these woven fabrics were similar to those of the convention ultrafine yarn without sleekness and dry feeling, and had a ratio of moisture adsorption ( $\Delta MR = 2\%$ ) similar to that of the conventional N6 fiber.

[0139]

#### Example 19

The polymer alloy fibers made in Examples 1 through 13 were formed into high-density plain weaves, and plain weave constituted from the aggregate of nanofibers was obtained similarly to Example 18. The plain weave showed peculiar adhesiveness when immersed in water. The plain weave was buffed to make a wiping cloth. The wiping cloth had higher wiping performance than a wiping cloth made from the conventional ultrafine fibers, showing satisfactory performance as a wiping cloth.

[0140]

#### Example 20

The polymer alloy fibers made in Examples 1 through 6 were mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching to form a

nonwoven fabric of entangled fibers having mass per unit area of  $750 \text{ g/m}^2$ . This nonwoven fabric was impregnated with a solution consisting of 13% by weight of a polyurethane compound (abbreviated as PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (abbreviated as DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the nonwoven fabric was subjected to alkali treatment in a 3% aqueous solution of sodium hydroxide ( $60^\circ\text{C}$ , bath ratio 1:100) for 2 hours, thereby to remove 99% or more of the copolymerized PET from the polymer alloy fibers, thereby to obtain a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU having thickness of about 1 mm. The nanofiber structure was buffed on one side thereof with a sand paper to reduce the thickness to 0.8 mm, and the other side of the nanofiber structure was processed with an emery buffer machine, thereby to form an artificially raised surface of the aggregate of nanofibers that was then dyed and finished to produce a suede-like synthetic leather. The article thus obtained had excellent appearance with no dyeing unevenness nor a problem in the mechanical properties. It also provided softer and finer touch compared to a synthetic leather product made by using the conventional ultrafine fibers. It also had good moisture adsorbing capability, thus resulting

in soft and moist touch like human skin which could not be provided by the conventional synthetic leather.

[0141]

#### Comparative Example 7

The N6/PE blended fiber made in Comparative Example 3 was mechanically crimped and was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching, thereby to form a nonwoven fabric of entangled fibers having mass per unit area of 500 g/m<sup>2</sup>. The nonwoven fabric of entangled fibers was impregnated with a solution consisting of 13% by weight of a polyurethane compound (PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the non-woven fabric was processed with tetrachloroethylene, thereby to obtain a nanofiber structure formed from the N6 ultrafine yarn and the PU having thickness of about 1 mm. One side of the nanofiber structure was buffed with a sand paper to reduce the thickness to 0.8 mm. The other side of the nanofiber structure was processed with an emery buffer machine, thereby to form an artificially raised surface of the aggregate of nanofibers that was then dyed and finished to produce a suede-like synthetic leather



product. The article thus obtained was nothing more than an imitation of suede, with hands no better than that of the synthetic leather made from the conventional ultrafine fibers.

[0142]

#### Example 21

The polymer alloy fibers made in Examples 1 through 6 were mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching so as to form a nonwoven fabric of entangled fibers having mass per unit area of 750 g/m<sup>2</sup>. This nonwoven fabric was impregnated with a solution consisting of 13% by weight of a polyurethane compound (PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the nonwoven fabric was subjected to alkali treatment in a 3% aqueous solution of sodium hydroxide (60°C, bath ratio 1:100) for 2 hours, so as to remove 99% or more of the copolymerized PET from the polymer alloy fibers, thereby to obtain a matrix of polishing material comprising a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU, with PU content of 40% by weight. The fibrous material was cut into two parts, and buffed on the surface with sand

papers having grades of JIS #240, #350 and #500. The fibrous material was then nipped by heating rollers which were coated with fluorocarbon resin and were disposed one upon another with a gap of 1.0 mm therebetween and kept at a temperature of 150°C, so as to press the fabric with a pressure of 0.7 kg/cm<sup>2</sup>. Then the fabric was cooled quickly with a quenching roller of surface temperature 15°C, thereby to obtain a texturing cloth with smoothed surface. Results of evaluating this texturing cloth under the conditions described below are shown in Table 13. This texturing cloth made the textured surface smoother with less scratches than in the case of one made from the conventional ultrafine yarns, thus demonstrating excellent texturing performance.

[0143]

<Evaluation of texturing: texturing of hard disk>

Work: A substrate made of a commercially available aluminum plate, coated with Ni-P plating and polished.

(Mean surface roughness was 0.28 nm)

Texturing conditions: The substrate was set on a texture apparatus and was textured under the following conditions.

[0144]

Abrasive particles: Slurry of free abrasive particles made of diamond having mean particle size of 0.1  $\mu$ m.

Dripping rate: 4.5 ml per minute

Rotation speed: 1000 rpm

Tape speed: 6 cm/min.

Texturing cycle: 300 cycles of horizontal vibration per minute with amplitude of 1 mm.

Number of samples: 30 substrates per trial

<Mean surface roughness Ra of work>

Surface roughness of 30 substrates per trial was measured using an atomic force microscope (AFM) available from Veeco Inc. that was surrounded by a sound insulator and installed in a clean room controlled to a temperature of 20°C and a relative humidity of 50%, to determine the mean surface roughness Ra. Measurement was made over an area of 5  $\mu\text{m}$  by 5  $\mu\text{m}$  around each of two points selected at symmetrical positions with respect to the center of the disk, located at a distance of half the radius from the center.

[0145]

<Number of scratches>

Number of scratches (X) on the surface of each sample was counted by observing under an interference microscope available from ZYGO Inc. Scratches were counted when the size was not smaller than 0.1  $\mu\text{m}$  by 100  $\mu\text{m}$ . Based on the measurements of 30 substrates per trial, scratch count  $\beta$  is defined as follows using a point  $y$  determined from the number of scratches.

[0146]

When  $X \leq 4$ :  $y = X$

When  $X \geq 5$ :  $y = 5$

$\beta = \sum y_i$  ( $i = 1$  to  $30$ )

$\sum y_i$  represents the total number of scratches for 30 samples.

[0147]

#### Comparative Example 8

The N6/PE blended fiber made in Comparative Example 3 was mechanically crimped and was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching, thereby to form a nonwoven fabric of entangled fibers having mass per unit area of 500 g/m<sup>2</sup>. The nonwoven fabric of entangled fibers was impregnated with a solution consisting of 13% by weight of a polyurethane compound (PU) including polyether-based polyurethane as the main component and 87% by weight of N,N'-dimethylformamide (DMF), and the PU was solidified in an aqueous solution having DMF content of 40% by weight. After washing in water, the nonwoven fabric was processed with tetrachloroethylene, thereby to obtain a matrix of polishing material comprising a nanofiber structure constituted from the aggregate of N6 nanofibers and the PU. The matrix of polishing material was processed similarly to Example 22, thereby to obtain a texturing cloth. Evaluation of this

texturing cloth showed  $R_a = 1.6$  nm and  $\beta = 32$ , indicating that this texturing cloth had poor texturing performance with lower smoothness of the textured surface and more scratches than in the case of the texturing cloth made from the aggregate of nanofibers.

[0148]

[Table 13]

	Raw yarn	$R_a$ (nm)	$\beta$ (counts/30 substrates)
Example 21	Example 1	0.09	2
	Example 2	0.09	2
	Example 3	0.10	2
	Example 4	0.18	3
	Example 5	0.09	2
	Example 6	0.09	2
Comparative Example 8	Comparative Example 7	1.60	32

[0149]

#### Example 22

The polymer alloy fiber made in Example 1 was mechanically crimped, and the crimped yarn was cut into fiber segments having a length of 51 mm, separated by means of carding, and was formed into a web with a cross-wrap webber. The web was subjected to needle punching so as to form a nonwoven fabric of entangled fibers having mass per unit area of 350 g/m<sup>2</sup>. This nonwoven fabric was subjected to alkali

treatment in a 3% aqueous solution of sodium hydroxide (60°C, bath ratio 1:100) for 2 hours, so as to remove 99% or more of the copolymerized PET from the polymer alloy fibers, thereby to obtain a nonwoven fabric of N6 nanofibers. Five disks 4.7 cm in diameter were cut out of the nonwoven fabric of N6 nanofibers and were placed one on another in a circular filter column, through which a bovine blood including white blood cells (5700 cells per micro liter) was caused to flow at a rate of 2 milliliters per minute. Duration before the pressure loss reached 100 mmHg was 100 minutes, and spherical cell removal ratio at this time was 99% or higher and lymph cell removal ratio was 60%, thus proving a capability to select the spherical white blood cells related to inflammation. This is supposedly the effect of the voids existing between the nanofibers.

[0150]

#### Example 23

A bovine blood serum including 15 milliliters of endotoxin was caused to flow through 0.5 g of the nonwoven fabric of nanofibers that had been made in Example 22 and sterilized in an autoclave, so as to evaluate the capability of adsorption (at 37°C, 2 hours). The concentration of endotoxin LPS decreased from 10.0 ng per milliliter to 1.5 ng per milliliter, indicating a high adsorption capability. This is supposedly because the active surface area of the

nylon nanofibers, that is far greater than that of the conventional nylon fibers, provides far more amino-terminals than in the conventional nylon fibers.

[0151]

#### Example 23

A spun-bonded nonwoven fabric was made using the same combination of polymers as in Example 13 and an apparatus shown in FIG. 18. Melting temperature was set to 225°C, spinning temperature was set to 230°C, and spinneret surface temperature was set to 217°C in the twin-screw extrusion-kneader 23. The spinneret of the same specifications as in Example 1 was used with discharge per orifice of 0.8 g per minute and the distance from the bottom surface of the spinneret to the cooling start point being set to 12 cm.

[0152]

The nonwoven fabric of polymer alloy thus obtained was treated in warm water of 60°C for 2 hours so as to remove 99% or more of the polymer soluble to hot water by dissolution, thereby to obtain a nonwoven fabric made from the PLA nanofibers. The diameter of the nanofiber single fiber by number average was 50 nm ( $2 \times 10^{-5}$  dtex). Fineness ratio of single fibers having fineness in a range from  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  dtex was 98% or more, and fineness ratio of single fibers having diameters that fall in a range from 45 to 74 nm was 70%.

[0153]

Example 24

The round braids formed from the aggregate of nanofibers made in Examples 1 to 6 were immersed in 15% by weight aqueous solution of polyurethane prepolymer (molecular weight from 3000 to 4000) consisting of hexamethylene diisocyanate and hexamethylene polycarbonate having a molecular weight of 1000, for 30 minutes. The round braids were taken out of the solution and were processed for the linking of the polyurethane prepolymer at 120°C for 20 minutes. This process caused the polyurethane prepolymer that infiltrated into the voids between the nanofibers to become insoluble through the linking reaction, thereby to form a multi-component material consisting of linked polyurethane and the N6 nanofibers. The multi-component material having a shape of round braid had high stretching capability and specific surface touch of sticking nature.

[0154]

Example 25

The round braids of the aggregate of nanofibers made in Examples 1 to 6 were immersed in an ion exchange water, to which 1, 2-bis(trimethoxysilyl)ethane was added and the solution was stirred for 3 hours. After being left to stand at the room temperature for 14 hours, the solution was stirred for 13 hours followed by another 14 hours of



standing at the room temperature and 7 hours of stirring thereby to polymerize silica. After washing in ion exchange water, the round braids were dried in air. Through this process, a N6/silica composite material having the form of cloth with the N6 nanofibers acting as a template was obtained. It was an excellent material that showed both sufficient rigidity and resilience. It was also a hybrid material that had good flame retarding property.

[0155]

#### Example 26

The N6/silica composite material obtained in Example 25 was fired at 600°C, so as to remove the N6 used as the template and obtain a silica sheet having numerous micropores of several tens of nanometers in diameter. The sheet showed excellent adsorbing and deodorizing capabilities.

[0156]

#### Example 27

A knitted fabric formed from the aggregate of polyester nanofibers made in Examples 9 to 13 were caused to absorb a moisture adsorbent SR 1000 (10% water dispersion) available from TAKAMATSU OIL&FAT CO., LTD. Processing conditions were such that 20%owf of the moisture adsorbent was used as a solid component, bath ratio was set to 1:20, processing temperature was 130°C and processing time was set to one hour. Absorbing ratio of this adsorbent by ordinary polyester

fibers is substantially 0%. However, this aggregate of polyester nanofibers showed 10% or higher absorbing ratio, thus providing a knitted fabric of polyester having a high ratio of moisture adsorption of  $\Delta MR = 4\%$  or more, which is comparable to or higher than that of cotton.

[0157]

#### Example 28

The nonwoven fabric of short polymer alloy fibers obtained in Example 20 was immersed in a 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:50) for 2 hours, thereby to remove 99% or more of the copolymerized PET, thereby to obtain a nonwoven fabric formed from the aggregate of N6 nanofibers.

A coating liquid of silicone polymer was prepared by dissolving a methyltrimethoxysilane oligomer ( $n = 3$  or  $4$ ) in a solution of isopropyl alcohol and ethylene glycol mixed in 1:1 proportion and adding 4% by weight of dibutyltin diacetate as a polymerization catalyst to the silane oligomer. A nonwoven fabric formed from the aggregate of N6 nanofibers was immersed in the coating liquid at 30°C for 20 minutes, so that the woven fabric was fully impregnated with the coating liquid. Then the woven fabric was taken out of the coating liquid and dried at 60°C for 2 minutes, 80°C for 2 minutes and 100°C for 2 minutes, while accelerating the polymerization of silicone, thereby to obtain the nonwoven

fabric wherein the N6 nanofibers were coated with the silicon polymer. It showed excellent water repellant property and flame retarding property.

[0158]

#### Example 29

The nonwoven fabric of short polymer alloy fibers obtained in Example 20 was immersed in a 3% aqueous solution of sodium hydroxide (90°C, bath ratio 1:50) for 2 hours, thereby to remove 99% or more of the copolymerized PET, thereby to obtain nonwoven fabrics formed from the aggregate of N6 nanofibers. The nonwoven fabrics showed high performance of water content of 160% or more of its weight and water retention ratio of 80% or more of its weight. The water content and water retention ratio were calculated by the following procedure. A sample immersed in a water tank to soak sufficiently for 60 minutes was weighed (Ag) after removing the water retained on the surface, then weighed (Bg) again after dewatered in a centrifugal dehydrator (dewatered for 7 minutes at 3000 rpm), and weighed again (Cg) after being dried at 105°C for 2 hours, with the measured data substituted in the following equations.

[0159]

$$\text{Water content (\%)} = (A - C) / C \times 100 (\%)$$

$$\text{Water retention ratio (\%)} = (B - C) / C \times 100 (\%)$$

This nonwoven fabric formed from the aggregate of N6

nanofibers showed specific stickiness when 15% or more water was included therein.

[0160]

Example 30

A base cloth for poultice was made by using the nonwoven fabric of the aggregate of N6 nanofibers made in Example 29. When a medicine was applied to the base cloth, it showed a high capability of absorbing the medicine and a high adhesiveness, thus making an excellent poultice.

[0161]

Example 31

A bag was made from the nonwoven fabric formed from the aggregate of N6 nanofibers made in Example 29, and a cold insulator wrapped in an inner bag was put into the bag, thereby to make an ice pack. Dew drops of condensed moisture were adsorbed by the nonwoven fabric used in the ice pack bag. Since the nonwoven fabric showed excellent adhesiveness, the ice pack did not come off the body part where it was applied, and was easy to handle.

[0162]

Example 32

Chemical contaminant removing capability of a nonwoven fabric, made from the aggregate of N6 nanofibers made in Example 29 using the polymer alloy fibers made in Example 1, was evaluated as follows. 5 g of sample was put at the

center of a Tedlar bag having a capacity of 0.01 m<sup>3</sup> (10 liters), and air was caused to flow therein, followed by the introduction of the chemical contaminant into the bag so that a predetermined concentration was attained. The contaminated air was successively sampled while monitoring the concentration of the chemical contaminant in the Tedlar bag with a gas chromatography.

[0163]

Capability of removing formaldehyde, trimethylamine, isovaleric acid and dioctyl phthalate as the chemical contaminant was evaluated, and high removing capability was demonstrated (FIG. 19 to FIG. 22).

[0164]

#### Comparative Example 9

A commercially available plain weave of PET was tested to evaluate the chemical contaminant removing capability similarly to Example 32, and substantially no removing capability was shown (FIG. 19 to FIG. 22).

[0165]

#### [Effect of the Invention]

The aggregate of nanofibers of the present invention which has a small spread of single fiber fineness values allows it to make a cloth having excellent hands and a high-performance texturing cloth that could not be achieved in the prior art.

[Brief Description of the Drawings]

FIG. 1 is a TEM micrograph showing a cross section of polymer alloy fibers according to Example 1 of the present invention.

FIG. 2 is a graph showing the spread of single fiber fineness values of the nanofibers according to Example 1 of the present invention.

FIG. 3 is a graph showing the spread of single fiber fineness values of the nanofibers according to Example 1 of the present invention.

FIG. 4 is an optical micrograph showing the state of side view of fibers of the aggregate of nanofibers according to Example 1 of the present invention.

FIG. 5 is an SEM micrograph showing the state of side view of fibers of the aggregate of nanofibers according to Example 1 of the present invention.

FIG. 6 is a TEM micrograph showing a cross section of fibers of an aggregate of nylon nanofibers according to Example 1 of the present invention.

FIG. 7 is a graph showing reversible elongation/contraction at absorbing water in Example 1 of the present invention.

FIG. 8 is a graph showing the spread of single fiber fineness values of ultrafine fibers according to Comparative Example 4.

FIG. 9 is a graph showing the spread of single fiber fineness values of ultrafine fibers according to Comparative Example 4.

FIG. 10 is a graph showing the spread of single fiber fineness values of the ultrafine fibers according to Comparative Example 5.

FIG. 11 is a graph showing the spread of single fiber fineness values of the ultrafine fibers according to Comparative Example 5.

FIG. 12 is a diagram showing a spinning machine.

FIG. 13 is a diagram showing a spinneret.

FIG. 14 is a diagram showing a drawing machine.

FIG. 15 is a diagram showing a spinning machine.

FIG. 16 is a diagram showing a spinning machine.

FIG. 17 is a diagram showing a spinning machine.

FIG. 18 is a diagram showing a spun bond spinning machine.

FIG. 19 is a graph showing the capability to remove formaldehyde according to Example 32.

FIG. 20 is a graph showing the capability to remove trimethylamine according to Example 32.

FIG. 21 is a graph showing the capability to remove isovaleric acid according to Example 32.

FIG. 22 is a graph showing the capability to remove dioctyl phthalate according to Example 32.

## [Description of Reference Numerals]

- 1: hopper
- 2: melting section
- 3: spin block
- 4: spinning pack
- 5: spinneret
- 6: cooling equipment
- 7: line of thread
- 8: thread-collecting finishing guide
- 9: first take-up roller
- 10: second take-up roller
- 11: wound yarn
- 12: weighing section
- 13: orifice length
- 14: orifice diameter
- 15: undrawn yarn
- 16: feed roller
- 17: first hot roller
- 18: second hot roller
- 19: third roller (room temperature)
- 20: drawn yarn
- 21: single-screw extrusion-kneader
- 22: static mixer
- 23: twin-screw extrusion-kneader
- 24: chip weighing machine



25: ejector

26: fiber separating plate

27: separated line of thread

28: collector

[Name of Document]        Abstract

[Abstract]

[Object]        To provide a polymer alloy fiber constituted from polymers having different levels of dissolution which are dispersed on the nanometer order therein, which can be preferably used as a precursor for nanofibers having less spread of single fiber fineness values that can be used in wide applications without limitation to the shape and the kind of the polymer.

[Solution Means]    The present invention is a polymer alloy fiber that has islands-in-sea structure consisting of two or more kinds of organic polymers of different levels of solubility, wherein the island component is made of a low solubility polymer and the sea component is made of a high solubility polymer, while the diameter of the island domains by number average is in a range from 1 to 100 nm, and 60% or more of the island domains have sizes in a range from 1 to 100 nm in diameter.

[Selected Drawing]        FIG. 1